

Structural anomalies, spin transitions and charge disproportionation in $LnCoO_3$

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The diamagnetic-paramagnetic and insulator-metal transitions in $LnCoO_3$ perovskites ($Ln = La, Y$, rare earths) are reinterpreted and modeled as a two-level excitation process. In distinction to previous models, the present approach can be characterized as a LS-HS-IS (low-high-intermediate spin) scenario. The first level is the local excitation of HS Co^{3+} species in the LS ground state. The second excitation is based on the interatomic electron transfer between the LS/HS pairs, leading finally to a stabilization of the metallic phase based on IS Co^{3+} . The model parameters have been quantified for $Ln = La, Pr$ and Nd samples using the powder neutron diffraction on the thermal expansion of Co-O bonds, that is associated with the two successive spin transitions. The same model is applied to interpret the magnetic susceptibility of $LaCoO_3$ and $YCoO_3$.

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The perovskite cobaltites $LnCoO_3$ ($Ln = La, Y$, rare-earth) systems show an insulating ground state based on the diamagnetic low spin state of trivalent cobalt (LS, $t_{2g}^6 e_g^0$, $S = 0$). With increasing temperature the systems undergo two magnetic transitions connected with excitations either to the intermediate spin (IS, $t_{2g}^5 e_g^1$, $S = 1$) or to the high spin state (HS, $t_{2g}^4 e_g^2$, $S = 2$).

Both transitions can be easily detected in the magnetic susceptibility in the case of parent compound $LaCoO_3$. The first transition starts at about 50 K and saturates at about 150 K where a new phase is stabilized with insulating character and Curie-Weiss susceptibility. The saturated paramagnetic phase is manifested by a linear part of the inverse susceptibility over the region 150 - 350 K that gives $\mu_{eff} \sim 3.2 \mu_B$ and AFM interactions characterized by $\theta \sim -200$ K. Recent experiments at low-temperatures, including electron spin resonance (ESR) [1], inelastic neutron scattering [2] and X-ray magnetic circular dichroism (XMCD) [3], identify the first transition as an excitation to HS state. The LS/HS scenario is also supported by band structure calculations [4, 5] that reveal three possible ground states for $LaCoO_3$ in the dependence of lattice volume and geometry: LS phase, LS/HS(1:1) ordered phase and homogeneous IS phase. The calculation evidence that the HS state is only stable if 6 nearest Co neighbors are in LS state, whereas stabilization of IS state is promoted by IS neighbors. HS states prefers antiferromagnetic interactions, whereas IS states prefers ferromagnetically aligned neighbors [5].

The second transition of an insulator-metal (I-M) kind starts at about 500 K and is accompanied with another increase of magnetic susceptibility and decrease of electric resistivity to a metallic value $\rho \sim 1$ mΩcm. Above the I-M transition, another region with quasilinear dependence of inverse susceptibility begins at about 600 K

and spreads up to 1000 - 1100 K. There is a clear change of slope with respect to region 150 - 350 K that is traditionally interpreted as an increase of effective moments of Co^{3+} while the strength of AFM interactions is retained (see *e.g.* Ref. [6]). We infer, however, that the observed susceptibility is a combined effect of a change of AFM interactions towards FM ones and onset of temperature independent Pauli paramagnetism, while the effective moments remain approximately the same.

This gives a possibility for a new interpretation of the spin transitions using the LS-HS-IS scenario: The diamagnetic-paramagnetic transition in $LaCoO_3$ originates in thermal population of HS states in LS matrix at about 50 K. Each Co^{3+} thus appears in a mixture of these two states with increasing probability of the HS one that saturates finally in the 1:1 ratio at about 150 K because of strong HS/LS nearest neighbor correlations. The second transition (I-M) starts above 350 - 400 K and should be related to a charge disproportionation [7, 8], in which t_{2g} electron transfer between LS/HS Co^{3+} neighbors, $LS Co^{3+} t_{2g}^6 e_g^0 + HS Co^{3+} t_{2g}^4 e_g^2 \rightarrow LS Co^{4+} t_{2g}^5 e_g^0 + HS Co^{2+} t_{2g}^5 e_g^2$, with charge transfer gap ~ 0.7 eV (see Fig. 5 in Ref. [5]), is an initial step. With increasing temperature, the probability of the electron exchange increases and new IS Co^{3+} states are gradually populated due to recombination reaction $LS Co^{4+} t_{2g}^5 e_g^0 + HS Co^{2+} t_{2g}^5 e_g^2 \rightarrow 2 IS Co^{3+} t_{2g}^5 e_g^1$. This opens an e_g conduction channel at about 500 K and leads finally to a formation of metallic phase of IS character that coexists with residual regions of LS/HS kind with fast dynamics. The optical conductivity data reveal indeed that this transition is associated with a collapse of the e_g charge transfer gap (originally ~ 2 eV) and the effect of high temperature is thus analogous to the effects of heavy doping in $La_{1-x}Sr_xCoO_3$ compounds [9]. The transitions temperatures for other $LnCoO_3$ compounds are increasing with decreasing Ln radius [10]. In particular, the onset of magnetic transition in $YCoO_3$ is shifted to 450 - 800 K and it develops concurrently with the I-M transition without reaching

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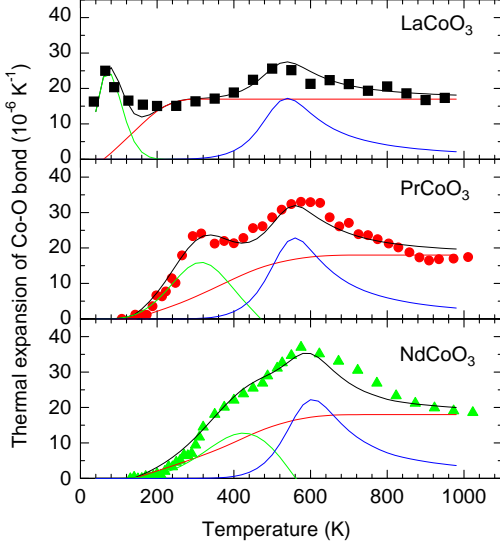


FIG. 1: Experimental (symbols) and fitted (lines) thermal expansion of Co-O bond for LaCoO_3 , PrCoO_3 and NdCoO_3 . The three contributions α^{latt} , α_1^{mag} and α_2^{mag} of the fitted thermal expansion are also displayed.

the saturated LS/HS (1:1) phase.

In the present paper we apply the LS-HS-IS model to interpret the thermal expansion of Co-O bonds of LnCoO_3 perovskites ($\text{Ln} = \text{La}, \text{Pr}$ and Nd) and quantify its parameters. The transitions are treated in a rather formal way as a two-level excitation from LS/LS pairs to LS/HS and IS/IS pairs. Since paramagnetic susceptibility is not sensitive to cobalt moments in systems with magnetic rare earths, the present analysis is primarily based on observed anomalies in thermal expansion that accompany both transitions due to the increasing ionic radius of Co^{3+} with increasing spin state [10, 11, 12, 13].

The thermal expansion data have been obtained by neutron diffraction experiments, performed at low temperature in LLB (Saclay, France) on the G41 diffractometer using a wavelength 2.422 Å and at high temperature in ILL (Grenoble, France) on the D20 diffractometer using a wavelength 1.361 Å. The observed neutron diffraction patterns were analyzed by a Rietveld method with the help of the FULLPROF program (Version 3.30 - Jun2005-LLB JRC). The magnetic susceptibility was measured on a SQUID magnetometer in the range up to 400 K using DC fields 10 kOe. The high temperature data up to 900 K were obtained using a compensated pendulum system MANICS in a field of 10 - 19 kOe.

The thermal expansion α of LnCoO_3 is a sum of three contributions: normal lattice expansion α^{latt} and anomalous expansions due to the two spin transitions α_i^{mag} .

(1) Lattice term α^{latt} is a weighted sum by populations $p_i(T)$ of thermal expansions of LnCoO_3 in individ-

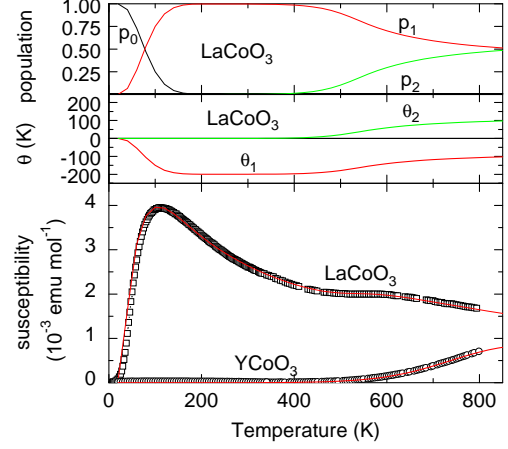


FIG. 2: Upper: Population of ground and excited states. Middle: Evolution of Weiss θ for excited states. Lower: Molar susceptibility for LaCoO_3 and YCoO_3 . The solid line is fit based on our model (see Eq. 7).

ual magnetic states

$$\alpha^{latt}(T) = \sum_{i=0}^2 p_i(T) \alpha_i^{latt}(T) \quad (1)$$

where $i = 0$ corresponds to ground state LS pairs, $i = 1$ is the first excited state LS/HS pairs and $i = 2$ means the second excited state IS pairs. Lattice thermal expansion increases with temperature and saturates around Debye temperature θ_D . In our analysis we have used the saturated values $\alpha_0^{latt} = 14 \times 10^{-6} \text{K}^{-1}$, $\alpha_1^{latt} = \alpha_2^{latt} = 18 \times 10^{-6} \text{K}^{-1}$, and Debye temperatures $\theta_D \sim 300$ K for LaCoO_3 and $\theta_D \sim 700$ K for the other LnCoO_3 .

(2) The anomalous contribution α^{mag} can be expressed as

$$\alpha_i^{mag}(T) = \frac{\partial p_i(T)}{\partial T} d_i^{mag}(T) \quad (2)$$

where d_i^{mag} is related to the difference between the size of ground and excited spin state and their dependence on temperature

$$d_i^{mag}(T) = d_i^{mag}(0) + \int_0^T \alpha_i^{latt}(T) - \alpha_0^{latt}(T) dT \quad (3)$$

In our fit we have found $d_1^{mag}(0) = 0.2\%$ and $d_2^{mag}(0) = 0.7\%$ for LaCoO_3 and $d_1^{mag}(0) = 0.3\%$ and $d_2^{mag}(0) = 1.0\%$ for the other LnCoO_3 .

Population of excited states p_i ($i=1, 2$) is calculated for each temperature point by solving the set of 2 equations

$$\frac{p_i(T)}{1 - \sum_{j=1}^2 p_j(T)} = \nu_i e^{-E_i/T} \quad (4)$$

where E_i is the energy difference between the ground and excited states in units of T , and ν_i is degeneracy of the

TABLE I: Ionic radii r_{Ln} for 9-fold coordination and the parameters of the thermal expansion fit for $Ln = \text{La, Pr and Nd}$ (see Eq. 5 and 6 for description of the parameters) and of the susceptibility fit for $Ln = \text{La and Y}$.

	r_{Ln}	E_1^o	T_o	n	E_2^o	E_2^p
	(Å)	(K)	(K)		(K)	(K)
LaCoO ₃	1.216	160	100	3.00	2 600	2 500
PrCoO ₃	1.179	890	370	3.11	2 700	2 600
NdCoO ₃	1.163	1 200	500	3.17	2 800	2 650
YCoO ₃	1.075	2 875	860	3.50	3 600	3 300

excited state. The ground state has $\nu_0 = 1$. For the first excited state $\nu_1 = 3$ can be anticipated for spin-orbit split state of HS Co³⁺ that is isolated in diamagnetic matrix while the spin degeneracy $\nu_1 = 2S + 1 = 5$ is more appropriate for concentrated LS/HS pairs. For the second excitation $\nu_2 = 2\nu_1$ was used.

The energy difference for the first excited state $E_1(T)$ depends on the structure changes induced by temperature [5] or by pressure [14]. In our analysis the dependence of energy $E_1(T)$ on temperature was arbitrarily fitted by a power function [10]

$$E_1(T) = E_1^o \left[1 - \left(\frac{T}{T_o} \right)^n \right] \quad (5)$$

where E_1^o is the energy splitting at $T = 0$ K, T_o is the temperature where $E_1(T_o) = 0$ and n is a fitting parameter that describes the curvature.

Since the stability of IS state is promoted by neighbors of the same kind, the energy $E_2(p)$ was set to depend on the concentration p_2 by the equation [7, 8]

$$E_2(p) = E_1(T) + E_2^o - E_2^p p_2^{1/3} \quad (6)$$

where E_2^o is the energy splitting for $p = 0$ and E_2^p describes the dependence on p_2 .

The experimental and calculated thermal expansion of Co-O bond for PrCoO₃ and NdCoO₃, completed with

data on LaCoO₃ taken from Ref. [11], are displayed in Fig. 1.

The susceptibility was fitted by an equation

$$\chi(T) = \frac{N_A \mu_B^2}{3k_B} \sum_{i=1}^2 \frac{\mu_i^2 p_i(T)}{T - \theta_i(T)} \quad (7)$$

where N_A is the Avogadro number, μ_B the Bohr magneton, k_B the Boltzmann constant and μ_i is the effective moment of corresponding excited state. The Weiss temperature θ was set to depend on the population of excited states $\theta_i(T) = \theta_i^o p_i(T)$. In our fit we have found $\theta_1^o = -200$ K, $\theta_2^o = +200$ K, $\mu_1 = \mu_2 = 3.25$ for LaCoO₃ and 2.93 for YCoO₃.

The temperature dependence of p_i and θ_i for LaCoO₃ and the experimental and calculated molar susceptibility for LaCoO₃ and YCoO₃ are shown in Fig. 2. The parameters of the thermal expansion fit (La, Pr, Nd) and of the susceptibility fit (La, Y) are summarized in Table I.

In conclusion, the diamagnetic-paramagnetic and insulator-metal transitions in $Ln\text{CoO}_3$ can be successfully explained within a model of two-level excitation. The first level is the excitation of HS Co³⁺ species in the LS matrix. The steep temperature decrease of the excitation energy close to the LS-HS crossover (T_o) is a signature that the local excitations lead finally to a global phase transition. The second excitation is based on the interatomic electron transfer and stabilization of IS Co³⁺ states. The present interpretation can be characterized as a LS-HS-IS scenario that is distinct from LS-IS-HS (or LS-LS/HS-IS/HS) models previously used.

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